

α,β -UNSATURATED SULFONYL COMPOUNDS IN THE
DIELS-ALDER REACTION

BY

HUGH VERITY ANDERSON

A.B., Kalamazoo College, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

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INTRODUCTION

Activated carbon to carbon double and triple bonds can add to conjugated dienes to produce cyclohexene derivatives. This reaction was correctly formulated in 1928 by Diels and Alder (1) and now bears their names. Although in the years since 1928 the reaction has received much attention (2), there were only two examples in the literature, when this investigation was begun, of such an addition to an ethylenic double bond activated by a sulfonyl group (3). Since that time one additional reaction of this nature has been reported (4).

It was the purpose of this study to prepare several *alpha-beta*-unsaturated sulfonyl compounds and to investigate their reactions with conjugated dienes.

DISCUSSION

Ethylenesulfonic acid has been prepared and subjected to the conditions of the Diels-Alder reaction with a variety of dienes. It causes the polymerization of 2,3-dimethyl-1,3-butadiene and of cyclopentadiene and it does not react with anthracene.

Ethylenesulfonyl chloride has been prepared and reacted with several dienes. It has been found to be very reactive towards butadiene and its homologs. Under comparatively mild conditions it reacted with 1,3-butadiene to give 4-cyclohexenesulfonyl chloride, with 2,3-dimethyl-1,3-butadiene to give 1,2-dimethylcyclohexene-4-sulfonyl chloride, with cyclopentadiene to give 2,5-methylene- Δ^3 -tetrahydrobenzenesulfonyl chloride, and with isoprene to give 1-methylcyclohexene-4 (or 3)-sulfonyl chloride. These adducts have been obtained in yields in the neighborhood of 90% and have been character-

ized as their sulfonamides or sulfonanilides. Ethylenesulfonyl chloride did not form an adduct with anthracene, furan, 2-ethyl-2-hexenalaniline, or 1-cyano-1,3-butadiene.

Methyl vinyl sulfone has been prepared and found to be slightly less reactive in the Diels-Alder reaction than ethylenesulfonyl chloride. It reacted with 1,3-butadiene to give 1,2,3,6-tetrahydrophenyl methyl sulfone, with 2,3-dimethyl-1,3-butadiene to give 3,4-dimethyl-1,2,5,6-tetrahydrophenyl methyl sulfone, with cyclopentadiene to give 2,5-methylene-1,2,5,6-tetrahydrophenyl methyl sulfone, and with isoprene to give 4 (or 3)-methyl-1,2,4,6-tetrahydrophenyl methyl sulfone. These adducts were obtained in yields in the neighborhood of 80% when the reactants were refluxed in benzene solution for four or more days.

Electronic theory predicts that the adducts formed from isoprene and these two dienophiles will have the sulfonyl group in the 4-position of the cyclohexene ring with respect to the methyl group. It has been impossible to confirm this prediction by experiment. Attempts to dehydrogenate these adducts have resulted in their destruction or have left them unchanged. An attempt to prove the structure of the isoprene-ethylenesulfonyl chloride adduct by synthesis has been unsuccessful.

Some exploratory work on the synthesis of other *alpha*, *beta*-unsaturated sulfonic acids has been carried out.

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VITA

The author was born in Chicago, Illinois, on August 25, 1921. He attended the public schools of Evanston, Illinois, graduating from Evanston Township High School in June, 1939. In the fall of that year he entered Kalamazoo College from which he was graduated in June, 1944, with the degree of Bachelor of Arts. Having enlisted in the Army in December, 1942, he was placed on active duty in February, 1943. He was discharged from the Army in November, 1945, and returned to Kalamazoo College to complete his undergraduate training. In the fall of 1946 he entered the Graduate College of the University of Illinois. He held a part time teaching assistantship from September, 1946, until June, 1949.



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